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Sampling of Automobile Interiors for Vinyl Chloride Monomer

Monsanto Research Corp, Dayton, Ohio

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SECTION I

INTRODUCTION

In recent years, some concern has developed over the concentrations of organic vapors in the interior of new automobiles. The principal sources of these organic pollutants are the plastics, rubbers, and adhesives that are extensively used in the interior of automobiles. The major volatilization products are unreacted monomers, plasticizers, and solvents trapped in the polymer during manufacture. The concentration of these compounds which are volatilized could exceed OSHA limits.

The purpose of this study was to obtain preliminary measurements of the concentration of vinyl chloride monomer (VCM) in the air in the interior of new automobiles. A literature search was also conducted to determine the expected volatilization products from plastics used in the construction of new automobile interiors.

SECTION II

SUMMARY AND CONCLUSIONS

Preliminary measurements were made of the vinyl chloride monomer (VCM) concentration in the interiors of seven different new 1975 automobiles. These were: Ford Pinto, Dodge Dart Sport, American Motors Gremlin, Volkswagen Rabbit, General Motors Vega, General Motors Chevrolet, and a Datsun 710. These compact and subcompact cars were selected because their ratio of plastic to interior volume was high and would be expected to result in worst-case concentrations for VCM.

Charcoal tubes were used to collect samples for VCM analysis. After drawing a known volume of air through each tube, the tubes were transported back to the laboratory for analysis by the NIOSH carbon disulfide extraction/gas chromatographic detection method.

Of the seven cars tested, only two, the Ford Pinto and the Dodge Dart, had measurable amounts of VCM in the interior atmospheres. These concentrations ranged from 0.4 ppm to 1.2 ppm. In the other five cars, the VCM concentrations were below the detection limit of the analytical system, 0.05 ppm.

These data indicate that concentrations of vinyl chloride monomer inside new cars rarely exceed the recommended exposure limit of one ppm, even in cases where the cars have received little or no ventilation. Calculation of the maximum one-time exposure to VCM in 1975 cars would not be expected to exceed 30 ppm, even assuming zero loss of VCM from the polyvinylchloride from its time of manufacture until the time when it was all released inside the unventilated car.

Volatilization of organic compounds from plastics used to construct automobile interiors was studied. A literature search was also conducted to determine the potential volatilization products from nineteen plastic and adhesive products typically used in automobile interiors. A total of 41 organic gases which volatilize from these products at temperatures of 25°C or 68°C were identified, ranging from methane to alcohols to linear phthalate esters. Six of the compounds identified are listed as suspected carcinogens: vinyl chloride, trichloroethylene, benzene, phenol, chloroform, and 1,4-dioxane.

SECTION III

LITERATURE SURVEY

A. VOLATILIZATION PRODUCTS OF PLASTICS

A literature survey was conducted to determine the potential volatilization products from the plastics used to construct the interiors of new automobiles. The majority of the plastics used for automobile interiors include ABS (acrylonitrile-butadiene-styrene), acrylic, polyethylene, polypropylene, polyurethane, and PVC (polyvinyl chloride). Plastics that are used in lesser quantities include alkyds, cellulosics, epoxies, fluoroplastics, melamine, noryl phenylene oxide-based resin, nylon, phenolic, polycarbonate, reinforced polyester, polystyrene, SAN (styrene-acrylonitrile), and thermoplastic polyester. The uses of these plastics are summarized in Table 1.

The volatilization products associated with these plastics were determined in a series of studies conducted by Pustinger, Hodgson, and co-workers of Monsanto Research Corporation.[1-5] In these studies, the off-gas products of a number of specific plastics compounds were measured at 25°C and 68°C. For the purpose of this report, no attempt was made to quantify these emissions because of varying sampling and analytical techniques used. A brief discussion of the off-gas products from specific plastic compounds is given below.

1. Acrylonitrile-Butadiene-Styrene (ABS)

In automobile interior construction, ABS finds extensive application in dashboard and instrument panel components and is used in conjunction with other plastics in seat assemblies, door and quarter panels, armrest assemblies, seat belts, plated hardware, vents and ducts, and as a structural base for assorted trim.

In an analysis of one type of commercial ABS polymer (Boltaron) eight volatilization products were identified at 25°C and six products at 68°C (Table 2). In both cases unreacted styrene monomer was the principal constituent.

In a study conducted by Harrison and Portwood,[6] various ABS materials were heated at temperatures of 49-90°C. Again styrene was the principal volatilization product, representing 95% (by weight) of the organics released.

TABLE 1. SUMMARY OF USES OF PLASTICS IN AUTOMOBILE INTERIORS

Plastics	Use
ABS (acrylonitrile-butadiene-styrene)	Dashboard, instrument panel components, seat assembly, door and quarter panels, armrest assemblies, seat belts, plated hardware, vents and ducts, structural base for assorted trim
Acrylic	Nameplates, dials, various instrument panel components
Epoxy	Adhesive for numerous components
Phenolic	Small quantity used as a sealant and adhesive
Polyester/glass	Heater and air conditioning housing
Polypropylene	Door panels, heater and air conditioning housing, station wagon decks, seat backs, dash panel inserts, sun visor, filler panels and other trim
Polyurethane	Cushioning material, trim, horn buttons, armrests, sun visor, crash pads
PVC (polyvinyl chloride)	Seat padding, seat upholstery, head liners, crash pad, sun visor, armrests

TABLE 2. ABS VOLATILIZATION PRODUCTS

At 25°C	At 68°C
Methane	Methane
Trichloroethylene	Trichloroethylene
Ethanol	Toluene
n-Propanol	Xylene
Toluene	Styrene
Xylene	Methylstyrene
Styrene	
Methylstyrene	

2. Acrylic

Acrylic plastics are used for nameplates, dials, and various other instrument panel components.

In an analysis of Plex 55 acrylic, only one volatilization product, methane, was identified at 25°C. At 68°C, three off-gas products were detected (Table 3). In both cases only low concentrations of volatiles were noted.

TABLE 3. VOLATILIZATION PRODUCTS OF PLEX 55 ACRYLIC

At 25°C	At 68°C
Methane	Methane
	n-Propanol
	Benzene

3. Epoxy

Epoxy resin adhesives are used throughout the interior of automobiles.

The literature yielded information on eight types of epoxy adhesives that have been tested for volatilization products. The results of these analyses vary widely. Several of the adhesive compositions had as many as nine off-gas products, while one of the compounds, epoxy Stycase 2651/catalyst II, was free of volatilization products.

Although the results from these analyses were difficult to quantify, the predominant volatilization products at 25°C were methane, ethanol, and xylene. In at least two of the compounds tested, xylene was detected in high concentrations. At 68°C the most common off-gas products were methane, ethanol, xylene, and acetone. A list of all possible volatilization products from epoxy adhesives is given in Table 4.

TABLE 4. VOLATILIZATION PRODUCTS FROM EPOXY ADHESIVES

At 25°C	At 68°C
(5)[a] Methane	(5) Methane
(1) 1,1,1-Trichloroethane	(1) 1,1,1-Trichloroethane
(1) Trimethylhexane	(2) C_4-C_6 Hydrocarbons
(1) Ethylene	(1) Ethylene
(1) Methanol	(1) Methanol
(4) Ethanol	(5) Ethanol
(3) n-Propanol	(2) n-Propanol
(1) Isopropanol	(1) Isopropanol
(1) 2-Methyl-1-propanol	(1) 2-Methyl-1-propanol
(2) n-Butanol	(2) n-Butanol
(1) Diethyl ether	(1) Diethyl ether
(3) Acetone	(4) Acetone
(3) 2-Butanone	(3) 2-Butanone
(1) 4-Methyl-2-pentanone	(1) 4-Methyl-2-pentanone
(1) 2-Methyl-4-pentanone	(1) 2-Methyl-4-pentanone
(3) Toluene	(3) Toluene
(4) Xylene	(4) Xylene
	(1) Benzaldehyde

[a]Number in parentheses denotes the number of epoxy compounds tested (out of a total of 8) which produced this volatilization product.

4. Melamine

Approximately twenty alcohols and aliphatic and aromatic hydrocarbons were identified as the volatilization products from two melamine compounds. The major off-gas compound at both temperatures was n-butanol, while xylene was also present in high concentrations at 25°C (Table 5).

5. Phenolic

In the construction of automobile interiors, phenolic resin is used in small quantities as a sealant and adhesive.

Volatilization products from three commercial phenolic compounds ranged from a mixture of seven aliphatic and aromatic hydrocarbons and ketones to methane alone (Table 6). The same volatiles were identified at 25°C and 68°C with the exception of methane, which was not detected at 25°C.

6. Polyester/Glass

Glass-reinforced polyesters are used in automobile interiors for heater and air conditioner housings.

TABLE 5. VOLATILIZATION PRODUCTS FROM TWO MELAMINE SAMPLES

At 25°C	At 68°C
(2)[a] Methane	(1) Methane
(1) C_4-C_6 Hydrocarbons	(2) C_4-C_6 Hydrocarbons
(2) C_7-C_8 Hydrocarbons	(2) C_7-C_8 Hydrocarbons
(1) C_9-C_{10}Hydrocarbons	(1) C_{10} Hydrocarbons
(2) Ethanol	(2) Ethanol
(2) n-Propanol	(2) n-Propanol
(1) 2-Propanol	(1) 2-Propanol
(1) 2-Methyl-1-propanol	(1) 2-Methyl-1-propanol
(2) n-Butanol	(2) n-Butanol
(1) Benzene	(1) Toluene
(1) Toluene	(2) Xylene
(1) C_3-C_5 Alkylbenzene	(1) C_3-C_5 Alkylbenzene
(2) Xylene	(1) Higher molecular weight alkylbenzenes
(1) Higher molecular weight alkylbenzenes	

TABLE 6. VOLATILIZATION PRODUCTS OF PHENOLIC COMPOUNDS

At 25°C and 68°C
(2)[a] Methane
(1) C_6-C_7 Hydrocarbons
(1) n-Propanol
(1) Furfuraldehyde
(1) Acetone
(1) Methyl ethyl ketone
(1) Benzene
(2) Toluene
(2) Xylene
(1) Phenol

[a]Number in parentheses denotes the number of phenolic compounds tested (out of a total of 3) which produced this volatilization product.

The volatilization products were identified in an analysis of two reinforced polyester products are listed in Table 7. Only small concentrations of acetone, benzene, and xylene were detected in off-gas products from both samples.

TABLE 7. VOLATILIZATION PRODUCTS FROM TWO POLYESTER/GLASS REINFORCED SAMPLES

At 25°C	At 68°C
C_7-Saturated hydrocarbons	Methane
2-Propanol	C_7-Saturated hydrocarbons
2-Methyl-2-propanol	n-Propanol
2-Butanol	2-Propanol
Acetone	2-Methyl-2-Propanol
Benzene	n-Butanol
Toluene	2-Butanol
Xylene	Benzene
	Toluene
	Xylene
	C_4-Alkylbenzene

7. Polypropylene

In authomobile interiors, reinforced polypropylene foam is used in quarter and door panels, heater and air conditioning housings, station wagon decks, seat backs, dash panel inserts, sun visors, filler panels, and miscellaneous trim. For many such applications, polypropylene is copolymerized with ethylene.

Emissions of volatilization products are reduced because unreacted propylene monomer, amorphous polymer, and reaction diluents are removed from the polypropylene during processing. Five volatilization products of Polypropylene 65-23 were identified (Table 8). With the exception of toluene, all of these volatile compounds were C_4-C_9 alkenes and were found in low concentrations. Emission species were quantitatively identical at both 25°C and 68°C.

Table 8. VOLATILIZATION PRODUCTS FROM POLYPROPYLENE 65-23

At 25°C and 68°C
Butene
Methyl butene
Dimethyl butene
Trimethyl hexadiene
Toluene

8. Polyurethane

Flexible and rigid polyurethane foams and all types of integral-skin foams are the most widely used plastics in automobile interiors. Flexible and rigid foams account for nearly all cushioning materials, while integral-skin polyurethanes are widely used in the trim. Flexible foams are used for horn buttons, armrests, and sun visors. Semirigid foams are used for crash pads.

Since so many different combinations of compounds are used in polyurethane formulations, volatile emissions vary considerably from one product to another. A total of fifteen volatilization products have been detected in the off-gas products from seven commercial polyurethane compounds (Table 9). At 25°C, ten different volatilization products were identified, but only methane, ethanol, n-butanol, toluene, and xylene were present in two or more polyurethane samples. At 68°C, only methane, ethanol, toluene, and xylene were emitted by more than one of the samples. Two of the polyurethanes tested, Spandex Lycra Polyurethane and Polyurethane PR 15-35, were free of volatiles.

TABLE 9. VOLATILIZATION PRODUCTS FROM POLYURETHANES

At 25°C	At 68°C
(4)[a] Methanol	(3) Methane
(3) Ethanol	(1) Chloroform[b]
(2) n-Butanol	(1) Methanol
(1) Acetone	(2) Ethanol
(1) Benzene	(1) n-Butanol
(4) Toluene	(1) 2-Methyl-2-butanol
(3) Xylene	(1) Acetone
(1) C_1-C_3 Alkylbenzenes	(1) Benzene
(2) 2-Phenyl-2-propanol	(3) Toluene
(1) Acetophenone	(2) Xylene
	(1) C_1-C_3 Alkylbenzenes
	(1) 2-Phenyl-2-propanol
	(1) Acetophenone
	(1) 1,4-Dioxane
	(1) n-Methyl morpholine

[a]Number in parentheses denotes the number of polyurethane compounds tested (out of a total of 7) which produced this volatilization product.

[b]Possibly carcinogenic.

9. Polyvinyl Chloride (PVC)

In the construction of automobile interiors, PVC sheet and foam find a wide variety of applications; they are second only to the polyurethanes in total consumption. PVC foam is used primarily for seat padding and undercovering, and PVC sheet is used for seat upholstering, head liners, crash pad skin, and facing for rear window panels, door inner panels, sun visors, and armrests.

An analysis of Boltaron 6200, Rigid PVC Type I for volatiles detected only three hydrocarbons at 68°C, and none at 25°C. However, it is suspected that unreacted vinyl chloride monomer may be a volatilization product of the plasticized PVC found in automobile interiors. It has been estimated[7] that vinyl chloride levels in PVC resins may range as high as 8000 ppm, although unreacted monomer concentrations are usually in the neighborhood of 50-1000 ppm. In finished products, this figure is probably reduced to 5-20 ppm.

Plasticizer volatilization is a recognized attribute of PVC products, and has been cited as the major cause of windshield fogging and "new car smell."[8] In automobile interior components, the linear phthalates are the most commonly used plasticizers, possessing better low-temperature properties than the more universally popular branched phthalates. Linear phthalate esters are based on linear C_6-C_{10} alcohols, and normally comprise 15-50% of a PVC product.

Phthalate ester concentrations on the order of 0.3 µg/liter have been measured in automobile interiors. However, this testing was conducted on a 1972 automobile and it is not known whether branched or linear phthalate plasticizers were involved. The linear phthalates are known to be 50-80% less volatile than their branched counterparts.

TABLE 10. VOLATILIZATION PRODUCTS FROM PVC

At 25°C	At 68°C
Vinyl chloride	Methane
Linear phthalate esters	C_4-C_5 Hydrocarbon
	Vinyl chloride
	Toluene
	Linear phthalate esters

10. Polystyrene and Styrene-Acrylonitrile (SAN)

Although no information was available on the volatilization products of polystyrene and styrene-acrylonitrile, data from ABS

materials suggest the possibility of unreacted styrene monomer volatilization.

11. Nylon, Polycarbonate, and Polyethylene

Tests conducted on polyethylene film and various nylon and polycarbonate products indicate that these materials are free of volatiles.

12. Alkyds, Cellulosics, Fluoroplastics, NORYL Phenylene-Oxide-Based Resin, and Thermoplastic Polyester

No information was found dealing with the ambient volatilization products of these materials. However, these compounds find very limited application in automobile interiors and probably do not contribute significantly to organic pollutant levels.

B. SUSPECTED CARCINOGENIC COMPOUNDS

One of the objectives of this project was to identify those volatilization products that are suspected carcinogens. Table 11 lists all volatilization products identified in the previous section with the suspected carcinogen compounds identified.[9]

TABLE 11. VOLATILIZATION PRODUCTS FROM PLASTICS USED IN THE INTERIOR OF 1975 AUTOMOBILES

Volatilization products at 25°C and 68°C	
Methane	Diethyl ether
Trichloroethane	Furfuraldehyde
Trimethylhexane	Acetone
C_4-C_{10} Hydrocarbons	Methyl ethyl ketone
Ethylene	2-Butanone
Vinyl chloride[a]	4-Methyl-2-pentanone
Trichloroethylene[a]	2-Methyl-4-pentanone
Butene	Benzene[a]
Methylbutene	Toluene
Dimethylbutene	Xylene
Trimethylhexadiene	Styrene
Methanol	Methylstyrene
Ethanol	C_1-C_5 Alkylbenzenes
2-Propanol	Higher MW alkylbenzenes
2-Methyl-2-propanol	2-Phenyl-2-propanol
n-Butanol	Acetophenone
2-Butanol	Linear phthaltate esters
Additional products at 68°C	
Chloroform[a]	Benzaldehyde
1,1,1-Trichloroethane	1,4-Dioxane[a]
2-Methyl-2-butenal	

[a]Suspected carcinogenic compounds[9]

SECTION IV

SAMPLING PROCEDURES

A. AUTOMOBILES SAMPLED

Arrangements were made with various automobile dealers in Dayton, Ohio to sample new 1975 model vehicles for vinyl chloride monomer (VCM). The test vehicles were selected to insure a broad spectrum of vehicle types and manufacturers were sampled. Subcompact and compact cars were tested because the ratio of plastic to interior volume was high and would result in a worst-case organic concentrations.

The seven 1975 automobiles selected for the test were a Ford Pinto, Dodge Dart Sport, American Motors Gremlin, Volkswagen Rabbit (Hatchback), General Motors Vega, General Motors Chevrolet (Station Wagon), and a Datsun 710. A description of each automobile tested is included in the data sheets in Appendix A. Each data sheet describes the interior and exterior colors of the vehicle as well as the date the vehicle was assembled and the data the samples were taken.

B. SAMPLE COLLECTION

In order to quantitatively sample for VCM charcoal tubes were used for collection.

Charcoal tubes purchased from SKC, Inc. (Pittsburgh, Pa.) (Figure 1) were used to collect VCM in the interior of each test automobile. Each glass collection tube was filled with 100 mg of charcoal. Tests were performed by drawing 3 liters of air through the tube at 50 ml/min. The tubes were then capped, stored in a freezer at -20°C, and transported to the laboratory for VCM analysis by an extraction/gas chromatographic technique.

Sampling runs were made with personal-type air samplers. Two electric Telmatic Air Samplers (Bendix Models 150 and C115) were modified with remote controls so they could be activated from outside of the test vehicle. The batteries used to power the pumps were also located outside of the vehicle. Each sampling pump was calibrated and adjusted for a constant flow rate of 50 ml/min. The sampling tubes were placed on the front seat next to the sampling pump and connected by short tubes to minimize the exposure of the sample to tubing materials before the gases got to the carbon sorbent.

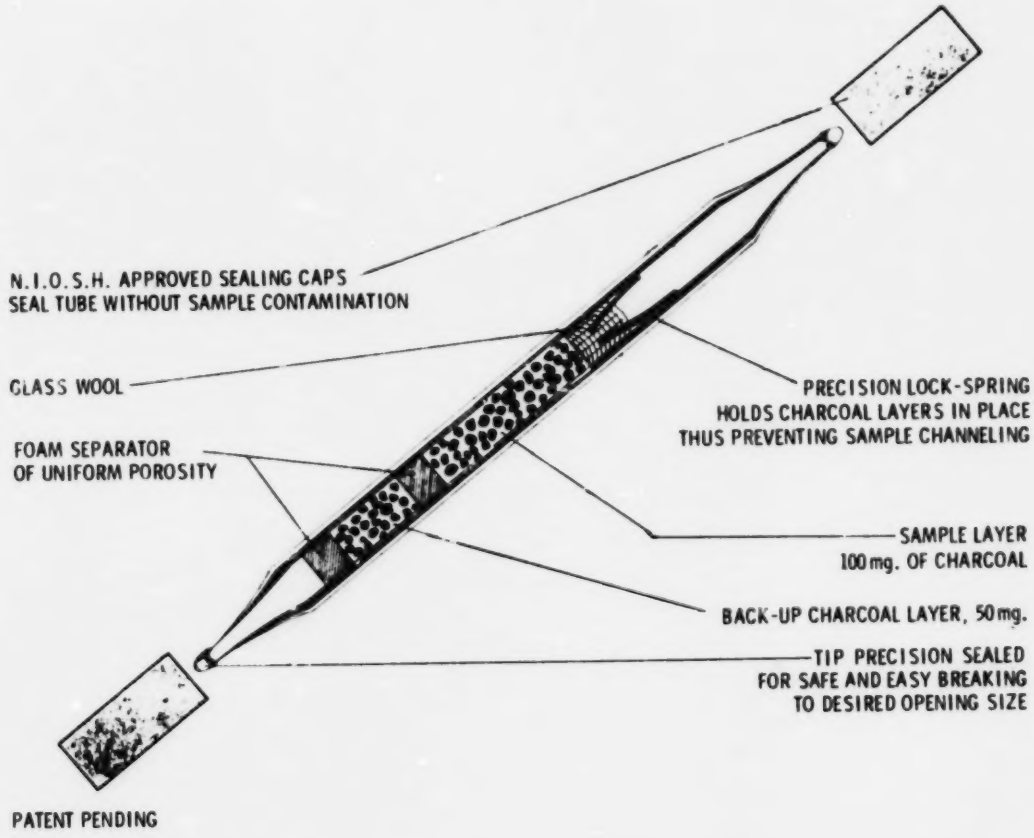

Figure 1. Charcoal tube used to collect VCM sample.

Each sampling package was equipped with a thermistor to measure the air temperature inside the test vehicle. An additional thermistor was used to measure the ambient temperature outside of the automobile.

The sample collection package was placed on the front seat, either on the driver's side or the passenger's side, wherever it appeared that the sun would heat the seat the most. It was reasoned that sampling the hottest seat during the hot summer time should establish a worst-case condition for pollutant concentrations. After placing the sampling package and inserting the collection tubes, the control wires for the samples were then run through the window, which was quickly rolled up to the top position. The seal at the top of the window was such that the window could be tightly closed and still allow the wires to pass through.

A period of at least 30 minutes was allowed to pass before sampling began in order to help reestablish equilibrium inside the car. Being aware that this time might not be sufficient to reach equilibrium, every effort was made to open the door carefully, slide the sampler in quickly, and close the door with minimum air interchange. This was always done from the downwind side to minimize ventillation in the car during this time. Unless over one-half of the air was changed during the sampler placement, the concentration read should be at least one-half of the maximum level, even if no additional vinyl chloride diffused out into the air space during the one-half hour waiting period before sampling. The actual amount of air interchange would be expected to be considerably less than this.

The sampling pumps were activated until approximately 3 liters of air had been sampled. The pumps were then turned off, and the collection tubes were quickly prepared for storage as previously described. The sampling conditions and the temperature of the seat, interior air, and exterior air are also shown on the data sheets in Appendix A.

SECTION V

SAMPLE ANALYSIS

The charcoal tubes were analyzed for VCM according to the technique described by the National Institute of Occupational Safety and Health (NIOSH), Method No. 178.[10] This procedure is given in Appendix B. Briefly, this method describes a procedure for determining quantitatively the amount of vinyl chloride in air by adsorption on charcoal and subsequent analysis by carbon disulfide extraction and gas chromatographic detection. This method also describes a procedure for determining the desorption efficiency of VCM from the charcoal by carbon disulfide extraction.

To determine the desorption efficiency, a standard solution of VCM and carbon disulfide was first prepared. A known concentration of 99.9% pure VCM was dissolved in a known volume of carbon disulfide as described in the Volumetric Method, Section 9.1 of NIOSH Method No. 178.[10] Various volumes of this solution were injected into a gas chromatograph equipped with a flame ionization detector and the response was recorded. A standard curve was prepared by plotting the known quantity of VCM versus the peak area recorded from the gas chromatograph response.

Next, a known concentration of VCM vapor was injected with a gastight syringe into a Tedlar* bag filled with a known volume of air. A charcoal tube was then attached to the bag outlet and a known volume of this air-VCM mixture was drawn through the charcoal tube. By using the air temperature and pressure, volume of air sampled, and VCM concentration in the Tedlar bag, the quantity of VCM absorbed by the charcoal tube could be calculated.

The charcoal was then extracted with carbon disulfide as described in NIOSH Method No. 178.[10] Known volumes of the extract were injected into the gas chromatograph and the response recorded. The peak areas obtained from these samples were compared to the standard curve to determine the quantity of VCM in the sample. The desorption efficiency was determined by dividing the quantity of VCM measured from the extract by the quantity of VCM calculated to be adsorbed in the charcoal tubes.

The desorption efficiency was measured three times using three concentrations of standard VCM gases. The standard gases had VCM

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*Fluorodynamics, Inc., Newark, Delaware.

concentrations of 1 ± 0.1 ppm, 10 ± 0.5 ppm, and 50 ± 1 ppm. These mixtures were purchased and certified by MG Scientific (Kearny, N.J.). For the batch of charcoal tubes used throughout this study, the desorption efficiency of VCM from the charcoal was determined by carbon disulfide extraction to be 31%, 31%, and 30% -- for an average of 31% -- and showed very good reproducibility. Though this percentage is not high similar measurements by other investigators have obtained readings of 18% for this measurement. Factors such as polymerization of VCM on the carbon and adsorption on vessel walls are suspected as being the primary causes for low desorption efficiencies when dealing with small amounts of VCM. These measurements were done at room temperature since the sample analyses were also done at these same conditions.

The minimum detectable limit for this gas chromatographic system for vinyl chloride was 0.75 ng per 5 µl injection. This resulted in a minimum atmospheric detection limit of 0.05 ppm for the sampling technique previously described.

The charcoal in the sampling tubes was divided into two parts (see Figure 1). The front half of the tube contained approximately 2/3 of the charcoal, while the back half contained the rest. After having a gas sample containing 500 micrograms of VCM passed through the tube, analysis of the back half of the tube revealed no VCM, meaning that the front half of the tube was 100% efficient at 23°C.

The question as to expected adsorption efficiency at higher temperatures might be raised. The actual sorption temperatures inside the cars ranged from 43°C to 66°C. To check the sorption efficiency of the carbon at the higher temperatures, the ratio of the equilibrium static absorptive capacity per unit weight of carbon at 65°C as compared to that at 25°C was calculated using the method recommended by Nelson and Harder.[11] This calculation indicates that the equilibrium static sorptive capacity for carbon at 65°C should be 18 percent as great as it is at 25°C. This is definitely more than adequate since the carbon in the first half of the tube completely adsorbed 500 micrograms of VCM during the test at 25°C and the three liter sample containing 1.2 ppm of VCM taken at elevated temperature contained only 2.6 micrograms of this material.

The gas chromatograph was equipped with a flame ionization detector and a 1.83 m x 0.21 cm column, packed with 80-100 mesh Chromosorb 102. A nitrogen carrier gas was used with a flow rate of approximately 30 ml/min.

Hydrogen (at 10 psig) was flowed at 25 ml/min and air (at 20 psig) was flowed at 110 ml/min to the flame ionization detector. The syringe injector port was maintained at 129°C, the oven at 127°C, and the detector at 119°C.

SECTION VI

RESULTS AND DISCUSSION

The results of the analyses of the charcoal tubes are shown in Table 12. The table indicates the make and model of the automobile tested, the temperature of the ambient air, interior air and seat surface, the number of days between the vehicle assembly and sampling dates, and the concentration of VCM detected. If VCM was not detected, then the VCM concentration was below the minimum detection limit of 0.05 ppm for the analytical system.

VCM was detected in only two of the seven automobiles tested, the Ford Pinto and the Dodge Dart. The higher concentration of VCM (1.2 ppm) found in the Ford Pinto may be due to a combination of the higher seat surface temperature (66°C) compared to the other vehicles tested and the relatively shorter period of time between vehicle assembly and sampling dates.

The concentration of VCM in the interior of a new automobile may be dependent on how frequently the vehicle is ventilated. Since it was not possible to control or quantify this variable, this could explain why VCM was detected in the Dodge Dart and not in the other five vehicles of comparable age. This conclusion is based on the assumption that the ratio of the vehicle interior volume to the quantity of polyvinyl chloride plastic is the same in each test vehicle. Data were not available to substantiate this assumption.

Since the level of VCM in 5 out of 7 of the test vehicles was below the detection limits of the analytical system, it was not possible to quantitatively develop a relationship between VCM volatilization emissions and the temperature of the seats or the age of the test vehicle. It also appeared that the interior and exterior colors of the automobile had no effect on the VCM emissions. The Ford Pinto had a black interior, but the Dodge Dart had a white interior. The darker interiors did, as expected, result in higher seat temperatures than did the lighter colored interiors.

The temperature to which the PVC plastic in the car is exposed should affect the rate at which VCM is emitted and the concentration level measured. A comparison of the seat temperatures and the VCM levels recorded in Table 12 does not show any correlation since all five of the cars with no measurable VCM concentration had higher seat temperatures than the Dodge Dart did.

Table 12. VCM IN THE INTERIOR OF 1975 AUTOMOBILES

1975 Automobile sampled	Temperature, °C			Number of days since vehicle assembly	Vehicle color		VCM concentration, ppm
	Ambient air	Interior air	Seat surface		Exterior	Interior	
Ford Pinto	36	60	66	32	Drk. red	Black	1.2
Dodge Dart: Front seat	27	50	46	102	Drk. red	White	0.4
Back seat	27	50	46	102			0.7
American Motors Gremlin	33	44	52	>60	Dr. Grn.	Drk. Grn.	<0.05[a]
Volkswagen Rabbit (Hatchback)	31	43	55	70	Red	Black	<0.05
General Motors Vega	33	45	49	>30	Lt. blue	Lt. blue	<0.05
General Motors Chevrolet (Station wagon)	33	45	49	120	Lt. brn.	Black	<0.05
Datsun 710	30	43	50	60	Drk. red	White	<0.05

[a]Minimum detectable limit of the analytical system.

PVC is a very stable material. Even when it does slowly decompose with age, it does not form more VCM. Hence the only VCM in the PVC in cars is that which was originally unreacted.

As the literature search revealed, the quantity of unreacted VCM remaining in a finished product constructed of PVC ranges from 5-20 ppm. An average automobile contains about 25 pounds of PVC. Therefore, the quantity of VCM trapped in the plastic would commonly be expected to range from 55 to 225 mg. If all of the VCM were volatilized at once into an automobile with 3 cubic meters of air space, this would result in VCM concentrations ranging from 7.2 to 29 ppm.

In conclusion, the data obtained in this study indicate that VCM concentrations in 1975 automobile interiors were in most cases below the recommended NIOSH standard of one ppm even in cars which were unventilated. With ventilation any car which contained a significant concentration, such as 1 ppm, would lose its VCM rather rapidly since the car would not be expected (by material balance) to be able to reestablish this concentration more than 7 to 29 times.

It should also be mentioned, however, that this was a preliminary screening study which was not intended to be rigorous or comprehensive. Though a variety of cars was sampled, data were collected from only one of each kind. Statistical variations within models were not examined in this study. Also, the effect of time between sampler placement in the car and the start of sampling was not investigated in this study. Due to the precautions taken (minimization of time the car door was open, entry from downwind side), the authors feel that this effect should be small, but no qualitative data on tis effect are available. Finally, the NIOSH method for vinyl cloride is intended primarily for use at room temperature. This method was used for this preliminary study because it is reasonably well defined, is familiar to workers in this field, and did not require any further development work.

If a more rigorous study were to be performed, the numbers of cars per model which would be sampled should be increased and the effects of equilibration time could be investigated. Though the authors feel that the results obtained in this study combined with the limited amount of VCM in PVC now being produced indicate that vinyl chloride in automobile interiors should not pose a significant health hazard, some consideration might be given to performing additional study to confirm this in 1976 cars in a more rigorous, comprehensive manner.

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APPENDIX A

DATA SHEETS

TABLE A-1. SAMPLING DATA

Automobile	
Manufacturer:	Ford Motor Co.
Model:	1975 Pinto 2-Door sedan
Colors:	Exterior dark red Interior black
Location:	Kettering, Ohio
Date assembled:	5-18-75
Date of arrival:	5-28-75
Date of sampling:	6-19-75
Sampling Conditions	
Pump:	Personnel air Sampling pump Bendix Model 150
Tube:	SKC charcoal tube
Ambient temperature:	36°C
Interior air temperature:	60°C
Seat surface temperature:	66°C
Last ventilated time:	6-18-75; 3:00 P.M.
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Front seat Back seat
Remarks	
Samplers placed in car at 2:00 P.M. Sampling began at 2:30 P.M. by remote switch.	

TABLE A-2. SAMPLING DATA

Automobile	
Manufacturer:	Chrysler Corp.
Model:	1975 Dart Sport
Colors:	Exterior dark red/white vinyl top Interior ivory white
Location:	Dayton
Date assembled:	4/1/75
Date of arrival:	4/15/75
Date of sampling:	7/15/75
Sampling Conditions	
Pump:	Bendix model 150
Tube:	SKC charcoal tube
Ambient temperature:	27.5°C
Interior air temperature:	50°C
Seat surface temperature:	46°C
Last ventilated time:	Approx. 30 min prior to sampling
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Passenger's seat Driver's seat

TABLE A-3. SAMPLING DATA

Automobile	
Manufacturer:	American Motors Corp.
Model:	Gremlin
Colors:	Exterior dark green Interior dark green
Location:	Dayton, Ohio
Date assembled:	No data
Date of arrival:	5/25/75
Date of sampling:	7/23/75
Sampling Conditions	
Pump:	Bendix model C115
Tube:	SKC charcoal tube
Ambient temperature:	33°C
Interior air temperature:	44°C
Seat surface temperature:	52°C
Last ventilated time:	30 min prior to sampling
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Driver's seat

Remarks

Battery went down after 40 min of sampling time

TABLE A-4. SAMPLING DATA

Automobile

Manufacturer:	Volkswagen
Model:	1975 Sedan 2-Door hatchback
Colors:	Exterior red Interior black
Location:	Dayton, Ohio
Date assembled:	5/15/75
Date of arrival:	7/2/75
Date of sampling:	7/24/75

Sampling Conditions

Pump:	Bendix model 150
Tube:	SKC charcoal tube
Ambient temperature:	31°C
Interior air temperature:	43°C
Seat surface temperature:	55°C
Last ventilated time:	30 min prior to sampling
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Driver's seat

Remarks

Pump was standard at 1:45 P.M.

TABLE A-5. SAMPLING DATA

Automobile

Manufacturer:	General Motors Corp.
Model:	1975 Vega
Colors:	Exterior light blue Interior light blue
Location:	Dayton, Ohio
Data assembled:	No data
Date of arrival:	7/1/75
Date of sampling:	7/25/75

Sampling Conditions

Pump:	Bendix model 150
Tube:	SKC charcoal tube
Ambient temperature:	33°C
Interior air temperature:	45°C
Seat surface temperature:	49°C
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Driver's seat

TABLE A-6. SAMPLING DATA

Automobile	
Manufacturer:	General Motors Corp.
Model:	1975 Chevrolet Station wagon
Colors:	Exterior white top w/wood grain sides Interior black
Location:	Dayton, Ohio
Date assembled:	4/1/75
Date of arrival:	4/15/75
Date of sampling:	7/29/75
Sampling Conditions	
Pump:	Bendix model 150
Tube:	SKC charcoal tube
Ambient temperature:	33°C
Interior air temperature:	45°C
Seat surface temperature:	49°C
Last ventilated time:	30 minutes
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Passenger's seat

TABLE A-7. SAMPLING DATA

Automobile	
Manufacturer:	Datsun
Model:	1975 Datsun 710
Colors:	Exterior dark red Interior white
Location:	Dayton, Ohio
Date assembled:	6/1/75
Date of arrival:	6/15/75
Date of sampling:	7/30/75
Sampling Conditions	
Pump:	Bendix model 150
Tube:	SKC charcoal tube
Ambient temperature:	30°C
Interior air temperature:	43°C
Seat surface temperature:	50°C
Last ventilated time:	30 min prior to sampling
Flow rate:	50 ml/min
Total volume:	3 liters
Location sampled:	Driver's seat

APPENDIX B

SAMPLING AND ANALYSIS OF VINYL CHLORIDE IN AIR[10]

VINYL CHLORIDE IN AIR

NIOSH Analytical Method

Analyte:	Vinyl Chloride (Chloroethene, Chloroethylene)	Method No :	P&CAM #178
Matrix:	Air	Range:	0.2-1500 ng per injection
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC		
Date Issued:	9/3/74	Precision:	Unknown
Date Revised:	10/15/74	Classification:	D (Operational)

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the vinyl chloride present.

   1.2 The charcoal in the tube is transferred to a small vial containing carbon disulfide where the vinyl chloride is desorbed.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   2.1 The minimum detectable amount of vinyl chloride was found to be 0.2 nanograms per injection at a 1 x 1 attenuation on a gas chromatograph.

   2.2 At the recommended sampling flow rate of 50 ml/min, the total volume to be sampled should not exceed 5.0 liters. This value is the volume of air containing 200 ppm of vinyl chloride which can be sampled before a significant amount of vinyl chloride is found on the backup section. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethan foam. (See Section 6.2.1) If a particular atmosphere

is suspected of containing a high concentration of contaminants and/or a high humidity is suspected, the sampling volume should be reduced by 50%.

3. Interferences

3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the capacity of the charcoal for organic vapors.

3.2 When two or more substances are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since these compounds may interfere with the analysis for vinyl chloride.

3.3 It must be emphasized that any compound which has the same retention time as vinyl chloride at the operation conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk material be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

The precision and accuracy of the total sampling and analytical method have not been determined.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more components suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 20% of that found on the front section, the possibility of sample loss exists. During sample storage, volatile compounds such as vinyl chloride will migrate throughout the tube until equilibrium is reached. At this time, 33% of these compounds will be found in the backup section. This may lead to some confusion as to whether sample loss has occurred. This migration effect can be considerably decreased by shipping and storing the tubes at -20°.

5.3 The precision of the overall method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal sampling pump for personal and area samples whose flow can be determined accurately at 50 milliliters per minute.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated coconut charcoal separated by a 2-mm portion of urethan foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing to remove material possibly absorbed on charcoal. The primary absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethan foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 ℓ/min.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Stainless steel column (20 ft x 1/8 in) packed with 10% SE-30 on 80/100 mesh Chromosorb W (acid washed, silanized with dimethyldichlorosilane). Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Two-ml vials which can be sealed with caps containing teflon-lined silicone rubber septa.

6.7 Microliter syringes: 10-μℓ, and convenient sizes for making standards.

6.8 Gas-tight syringes: 1-mℓ, with open/close valve.

6.9 Pipets: 0.5-mℓ delivery pipets or 1.0-mℓ type graduated in 0.1-mℓ increments.

6.10 Volumetric flasks: 10-mℓ or convenient sizes for making standard solutions. It is preferable to have plastic stoppers for the volumetric flasks.

7. Reagents

7.1 Spectroquality carbon disulfide.

7.2 Vinyl chloride, lecture bottle, 99.9% minimum purity.

7.3 Toluene, chromatographic quality.

7.4 Bureau of Mines Grade A helium.

7.5 Prepurified hydrogen.

7.6 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube are broken to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a backup and is positioned nearest the sampling pump.

8.3.3 The charcoal tube is placed in a vertical position during sampling to prevent "channelling" of the charcoal.

8.3.4 Air being sampled is not to be passed through any hose or tubing before entering the charcoal tube.

8.3.5 Bulk air samples (i.e., samples of 10-20 liters of the air in the environment) are taken along with personal samples.

8.3.6 The flow, time, and/or volume must be measured as accurately as possible. The sample is taken at a flow rate of 50 ml/min. The maximum volume to be sampled should not exceed 5.0 liters (See Section 2.2).

8.3.7 The temperature and pressure of the atmosphere being sampled is measured and recorded.

8.3.8 The charcoal tubes are capped with the supplied plastic caps immediately after sampling. Under no circumstances are rubber caps to be used.

8.3.9 One tube is handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube is labeled as a blank.

8.3.10 Capped tubes are packed tightly before they are shipped to minimize tube breakage during transport to the laboratory. If the samples will spend a day or more in transit, cooling (e.g., with dry ice) is necessary to minimize migration of vinyl chloride to the backup section.

8.3.11 Samples received at the laboratory are logged in and immediately stored in a freezer (around -20°) until time for analysis. Samples may be stored in this manner for long periods of time with no appreciable loss of vinyl chloride (2 months). Even around -20°C, vinyl chloride will equilibrate between the two sections of charcoal, i.e., will migrate to the backup section. This phenomenon is observable after two weeks and may be confused with sample loss after 1 to 2 months.

8.4 Analysis of Samples

8.4.1 Preparation and Desorption of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small vial containing 1 ml of carbon disulfide. (Note the addition to the CS_2 is important.) The vial is topped with a

septum cap (See Section 6.6). The separating section of foam is removed and discarded; the second section is transferred to another small vial containing 1 ml of CS_2. These two sections are analyzed separately. Tests indicate that desorption is complete in 30 minutes if the sample is agitated occasionally during this period. In any case samples should be analyzed within 60 minutes after addition to CS_2.

8.4.2 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 40 cc/min (80 psig) helium carrier gas flow
2. 65 cc/min (20 psig) hydrogen gas flow to detector
3. 500 cc/min (50 psig) air flow to detector
4. 230°C injector temperature
5. 230°C manifold temperature (detector)
6. 60°C isothermal column temperature (oven).

8.4.3 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10-µl syringe is first flushed with solvent several times to wet the barrel and plunger. Two microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent and the plunger is pulled back about 0.4 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn to the 7.4 µl mark (2 µl solvent + 0.4 µl air + 5 µl sample = 7.4 µl). After the needle is removed from the sample and prior to injection the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard are made. No more than a 3% difference in area is to be expected.

8.4.4 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of vinyl chloride that is removed in the

desorption process. Desorption efficiency should be determined on the same batch of charcoal tubes used in sampling. Results indicate that desorption efficiency varies with loading (total vinyl chloride on the tube), particularly at lower values, i.e., 2.5 µg.

8.5.2 Procedure for determining desorption efficiency. Charcoal tubes from the same batch as that used in obtaining samples are used in this determination. A measured volume of vinyl chloride gas is injected into a bag containing a measured volume of air. The bag is made of Tedlar (or a material which will retain the vinyl chloride and not absorb it) and should have a gas sampling valve and a septum injection port. The concentration of the bag may be calculated knowing room temperature and pressure. A measured volume is then sampled through a charcoal tube with a calibrated sampling pump. At least five tubes are prepared in this manner. These tubes are desorbed and analyzed in the same manner as the samples (See Section 8.4). Samples taken with a gas tight syringe from the bag are also injected into the GC. The concentration in the bag is compared to the concentration obtained from the tubes.

The desorption efficiency equals the amount of vinyl chloride desorbed from the charcoal divided by the quantity of vinyl chloride contained in the volume of synthetic atmosphere sampled, or

$$\frac{\text{quantity vinyl chloride from charcoal}}{\text{concentration vinyl chloride in atmosphere} \times \text{volume atmosphere sampled}}$$

9. Calibration and Standards

CAUTION: Laboratory Operations Involving Carcinogens

Vinyl chloride has been identified as a human carcinogen and appropriate precautions must be taken in handling this gas. The Occupational Safety and Health Administration has promulgated regulations for the use and handling of vinyl chloride. They may be found in 29 CFR 1910.93q (Section 1910.93q in Title 29 of the Code of Federal Regulations available in the Federal Register, Vol. 39, No. 194, Friday, October 4, 1974, pp. 35890-35898).

A series of standards, varying in concentration over the range of interest, are prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in µg/1.0 mℓ versus peak area. There are two methods of preparing standards and as long as highly purified vinyl chloride is used, both are comparable.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the FID response.

9.1 Standard Preparation

Gravimetric Method - Vinyl chloride is slowly bubbled into a tared 10-ml volumetric flask containing approximately 5 ml of toluene. After 3 minutes, the flask is again weighed. A weight change of 100-300 mg is usually observed. The solution is diluted to exactly 10 ml with carbon disulfide and is used to prepare other standards by removal of aliquots with different sized syringes. Subsequent dilution of these aliquots with carbon disulfide results in a series of points that are linear from the range of 0.2 nanograms per injection, the minimum detectable amount of vinyl chloride, to 1.5 micrograms per injection.

Volumetric Method - A 1-ml gas sample of pure vinyl chloride is drawn into a gas-tight syringe and the tip of the needle is inserted into a 10-ml volumetric flask containing approximately 5 ml of CS_2. The plunger is withdrawn slightly to allow the CS_2 to enter the syringe. The action of the vinyl chloride dissolving in the CS_2 creates a vacuum and the syringe becomes filled with the solvent. An air bubble (~2%) is present and was found to be due to the void volume in the needle of the syringe. The solution is returned to the flask and the syringe is rinsed with clean CS_2 and the washings added to the volumetric. The volumetric is then filled to the mark with CS_2. Other standards are then prepared from this stock solution.

Standards are stored in a freezer at -20°C and are found to be stable at this temperature for three days. Tight-fitting plastic tops on the volumetrics seem to retain the vinyl chloride better than ground glass stoppers.

10. Calculations

10.1 The weight, in µg, correspondong to each peak area is read from the standard curve for vinyl chloride. No volume corrections are needed, because the standard curve is based on µg/1.0 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank are made for each sample.

$$\mu g = \mu g_s - \mu g_b$$

where:

μg_s = µg found in front section of sample tube
μg = µg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 These values are further corrected for the desorption efficiency at the level of vinyl chloride measured.

$$\text{Corrected } \mu g = \frac{\mu g}{\text{desorption efficiency}}$$

10.4 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total amount of vinyl chloride in the sample.

10.5 The concentration of the vinyl chloride in the air sampled is expressed in mg/m^3, which is numerically equal to µg/liter of air

$$mg/m^3 = \mu g/\ell = \frac{\text{total } \mu g \text{ (Section 10.4)}}{V}$$

where:

V is the volume of air sampled

10.6 Another method of expressing concentration is ppm, defined as µℓ of vinyl chloride gas/liter of air

$$ppm = \mu g/\ell \times \frac{24.45}{62.5} \times \frac{760}{P} \times \frac{T+273}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (ℓ/mole) at 25°C and 760 mm Hg
62.5 = molecular weight (g/mole) of vinyl chloride
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

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